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PLASMA DEPOSITION OF ALTERNATE TiN/ZrN MULTILAYER HARD COATINGS

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Microchemical, microstructural, mechanical and tribological characteristics of alternate TiN/ZrN multilayer coatings were investigated by energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD), microhardness and thickness measurements, adhesion and wear resistance tests. The coatings, with various bilayer periods and thicknesses of the individual layers, were deposited on Si and steel substrates by the cathodic arc technique. A comparison with TiN and ZrN monolayer properties was carried out.

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1. Introduction

Multilayer structures have been used for many years in the coating technology for improving the performance of hard coatings for various machining applications [1-5]. Due to the complex requirements for the materials used as protective coatings such as high hardness, good adhesion at the substrate, low reactivity and friction with the materials in contact, an optimum solution seems to be a multilayer coating. An ideal coating structure consists of an inner layer with a good adhesion, one or more intermediate layers having high hardness, strength and toughness and an outer layer with a low reactivity and friction coeficient [6]. In recent years, nanometer scale multilayered hard coatings proved to be very attractive for wear-corrosion protection of materials. Some of these coatings, nowadays called heterostructures or superlattices, such as alternate TiN/AlN, TiN/NbN or TiN/VN coatings exhibited very high hardness (>50 GPa) and offer potential advantages for dry milling, drilling and turning. For other bilayer combinations (TiN/CrN, TiN/MoN, TiAlN/ZrN), maximum microhardness values did not exceed 30 GPa, but they are still interesting for tribological applications.

This paper reports the results of the investigation of alternate TiN/ZrN multilayer coatings prepared under different deposition conditions by the cathodic arc method. The films were analyzed in terms of phase composition, texture, microhardness, adhesion, deposition rate and wear resistance. For the individual layers TiN and ZrN, elemental composition was determined. Some preliminary experiments on wear resistance of the coatings were also performed. A comparison with the properties of TiN and ZrN single layer coatings was made.

2. Experimental

A schematic diagram of the deposition setup [7] is shown in Fig. 1. The system was equipped with two arc evaporators (cathodes) made of Ti and Zr. The coatings were deposited on different substrate materials: Si, stainless steel and high-speed steel. Specimens to be coated were ultrasonically cleaned with trichloroethylene and mounted on a rotating holder inside the chamber. Prior to

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deposition, the samples were sputtered by Ti or Zr ion bombardment (1000 V; 5 min.). For the TiN/ZrN multilayer preparation, rotating shutters placed in front of each cathode were used. The shutters were opened and closed so that Ti and Zr atoms were periodically introduced in the reactive atmosphere. Depending on the deposition rate of the individual layers (TiN and ZrN) and on the rotating speeds of the shutters, various multilayer configurations (with different thicknesses of the individual layers) could be prepared.

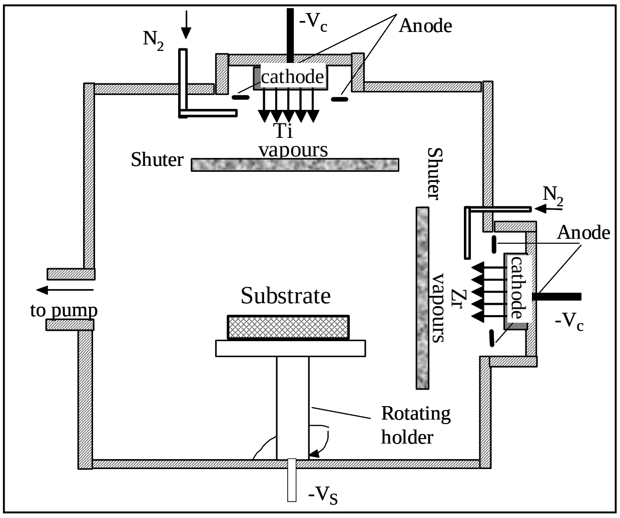


Fig. 1. Schematic illustration of the deposition setup.

The chemical composition of TiN and ZrN films was determined by energy – dispersive X-ray (EDX) spectroscopy, by means of a XL–30–ESEM TMP scanning electron microscope. Phase composition and texture were obtained by X-ray diffraction (XRD) analysis using an X-ray DRON diffractometer with CuK_{α} radiation. Microhardness measurementd were prtformed using a Wolpert microhardness tester (30g load). Film thickness was determined by optical microscope examination of the cross sections through the coatings. Scratch tests under standard condition were used to evaluate the coating adhesion. The critical load (L_c) was determined by optical microscopy. For the wear resistance investigations, a testing apparatus consisting of a coated rotating roller pressed on a flat specimen was used [7]. The testing parameters were: roller – 40 mm in diameter and 8 mm in width, made of stainless steel; sliding speed – 0.3 m/s, load – 10 N; environment – salt water (10 g/l). The wear behavior was appreciated by the maximum slideng distance L_{max} (the distance at which the damage of the coating occurs, commonly associated with a marked increase of the friction coefficient).

The bilayer period Λ was calculated from the overall thickness of the multilayer and the number of the layers. The thickness of the individual layers was obtained from the deposition rate and deposition time for each layer.

3. Results and discussion

Two sets of multilayer configurations were prepared. For the first series (samples 3-4, Table 1), the ratio between the thicknesses of the TiN and the ZrN films in the bilayer structure was of about 0.6, whereas for the second series (samples 7-8), the ratio was 1.5.

Table 1. Deposition parameters for single-layer and multilayer coatings I_{Ti} – current at the Ti cathode, I_{Zr} – current at the Zr cathode, p_{N3} – nitrogen pressure, V_s – substrate bias, t_i – deposition time for an individual layer.

Sample No	Coating	Deposition parameters				
		I_{Ti} (A)	I_{Zr} (A)	p_{N2} (Pa)	V_s (V)	t_i (sec)
1	TiN	90	-	10^{-1}	220	3600
2	ZrN	-	120	10^{-1}	220	3600
3	TiN/ZrN	90	120	10^{-1}	220	300
4	TiN/ZrN	90	120	10^{-1}	220	2.25
5	TiN	120	-	10^{-1}	220	3600
6	ZrN	-	100	10^{-1}	220	3600
7	TiN/ZrN	120	100	10^{-1}	220	300
8	TiN/ZrN	120	100	10^{-1}	220	2.25

Since the deposition time for each individual layer in a certain multilayer was constant, various thicknesses of the layers were obtained by using different currents at the Ti and Zr cathodes. The other deposition conditions (N_2 pressure, substrate bias) were selected from preliminary experiments, in order to obtain monolayer coatings of TiN and ZrN with high microhardness and good adhesion. The main processing parameters both for single layer and multilayer coatings are summarized in Table 1. Total deposition time for each coating was of 1 h.

3.1. Elemental composition, phase composition and texture

The elemental compositions of TiN and ZrN monolayer coatings were obtained by EDX analysis. An example of an EDX spetrum for a TiN coating (sample 1, Table 1) is given in Fig. 2. For the samples 1 and 2, the elemental compositions are presented in Table 2. It can be seen that the coatings are almost stoichiometric: N/Ti = 1.1 (sample 1); N/Zr = 0.9 (sample 2). The presence of a small amount of oxygen is probably due to the contamination during sample handling in open atmosphere before the composition analysis.

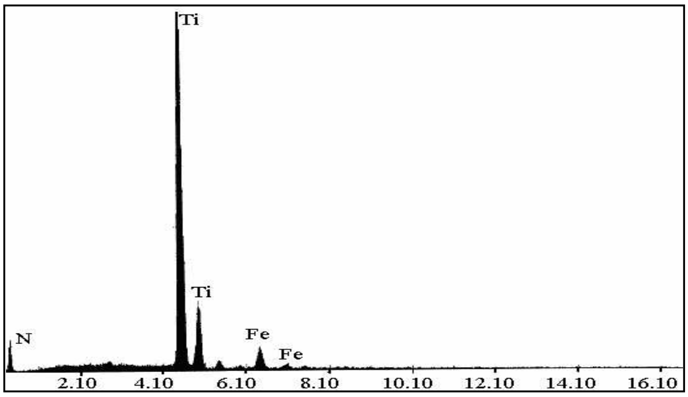


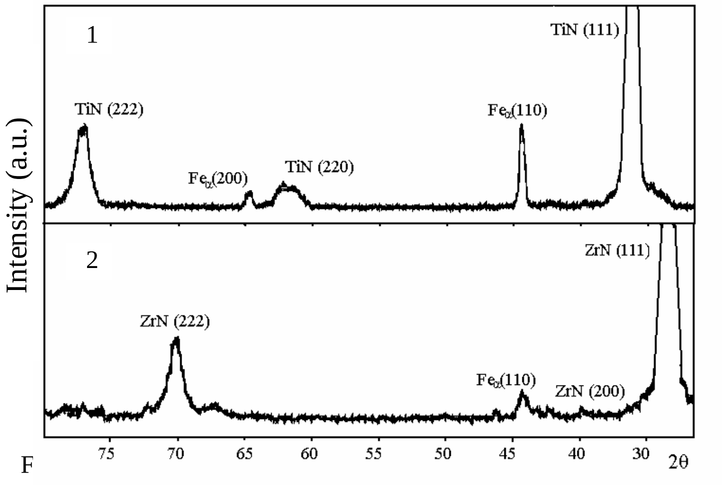
Fig. 2. EDX spectrum for a TiN coating.

Table 2. Elemental composition of TiN and ZrN coatings.

Sample No	Coating	Elemental concentration %				
		Ti	Zr	Fe	N	O
1	TiN	44.9	-	0.7	51	3.4
2	ZrN	-	49.6	0.9	44.8	4.7

Typical X-ray diffraction patterns for TiN and ZrN coatings (samples 1 and 2) can be examined in Fig. 3. One may observe a strong (111) preferred orientation, as it was commonly reported for the films deposited by this method [9,10]. This particular orientation was predicted under the deposition conditions in which the strain energy was dominant as compared to the surface energy [11].

For the multilayer TiN/ZrN coatings (samples 3 and 4), for which the ratio between the TiN and the ZrN film thicknesses was of about 0.6 (see Table 3), the diffraction patterns depends on the bilayer period (Fig. 4). For a high value of the bilayer period (450 nm, sample 3), one can observe the (111) lines, arising both from the ZrN and from the TiN coatings. As it was expected, due to the difference in the thicknesses of the individual layers, more intense ZrN lines were observed. For a bilayer period in the nanometer range (3.4 nm, sample 4), a different diffraction pattern was found: only one strong (111) peak, belonging to ZrN compound (2θ = 33.9°), was detected.



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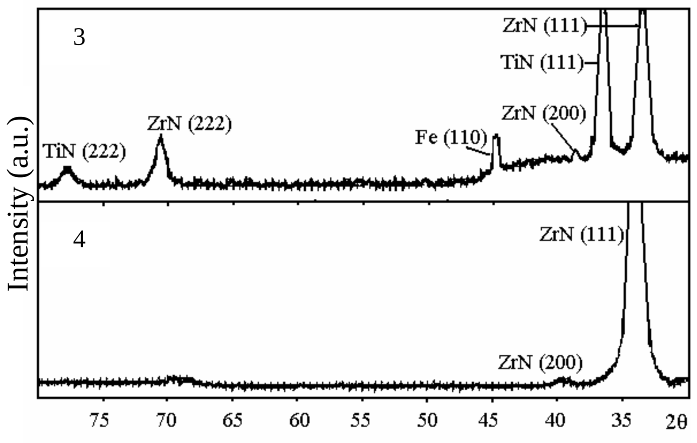

Fig. 4. X-ray diffraction patterns for multilayer TiN/ZrN coatings.

3.2. Mechanical characteristics

The results of the measurements of the mechanical properties of the coatings (mono and multilayer structured), deposited under the conditions given in Table 1, are summarized in Table 3. Deposition rate D_R, bilayer period Λ, thickness of an individual layer d_{TiN} (or d_{ZrN}), number of monolayers n_L, microhardness $HV_{0.03}$ and critical load L_c were determined.

It can be seen that the TiN coatings are harder than the ZrN coatings, as it was generally reported in many works (e.g. [6]). On the other hand, a better adhesion was found for the ZrN coatings (of all coatings, the highest values of the critical load were measured for the ZrN films).

A multilayer structure led to an increase of the microhardness, as compared to the TiN or ZrN monolayers. Moreover, the superlattice coatings ($\Lambda < 10$ nm, samples 4 and 8) exhibited the highest microhardness values. Nevertheless, superhard (>4000 HV) multilayer coatings were not obtained, in contrast with the TiN/AlN, TiN/NbN or TiN/HfN heterostructures [1] – [3], (under our deposition conditions, the maximum microhardness was of about 3000 $HV_{0.03}$). No systematic dependence of the adhesion on the bilayer period or on the individual film thickness was evidenced. Further experiments will be focused on the characteristics of the coatings with bilayer periods in the range 1 – 9 nm.

Table 3. Mechanical characteristics of single-layer and multilayer coatings.

Sample No	Coating	Mechanical charactereristics						
		D_r (nm/s)	Λ (nm)	d_{TiN} (nm)	d_{ZrN} (nm)	n_L	$HV_{0.03}$	L_c (N)
1	TiN	0.5	-	1800	-	1	2130	48
2	ZrN	0.9	-	-	3240	1	1920	53
3	TiN/ZrN	0.75	450	165	285	12	2560	40
4	TiN/ZrN	0.75	3.4	1.3	2.1	1600	2810	44
5	TiN	0.9	-	3240	-	1	2180	46
6	ZrN	0.6	-	-	2160	1	1840	56
7	TiN/ZrN	0.8	480	290	190	12	2280	50
8	TiN/ZrN	0.8	3.6	2.2	1.4	1600	3060	38

3.3. Wear resistance

A comparison between the wear resistance of the single layer coatings (TiN and ZrN) and of a multilayer structure (TiN/ZrN, with 12 layers) was made. The coatings investigated were the coatings 1, 2 and 3 from the Table 1. The maximum sliding distances are given in Table 4.

Table 4. Maximum sliding distance L_{max} for TiN, ZrN and TiN/ZrN coatings.

Sample No	Coatings	L_{max} (m)
1	TiN	2500
2	ZrN	2500
3	TiN/ZrN	6300

It can be seen that the TiN and Zr coatings exhibit the same wear resistance, though the TiN film is harder that the ZrN one. A significantly better behavior was found for the multilayer coating. As compared with the monolayers, the maximum sliding distance incresead 2.5 times. Further experiments will be performed in order to investigate the influence of the bilayer period on the wear behavior of the multilayers.

4. Summary and conclusions

Characteristics of alternate TiN/ZrN multilayers hard coatings, with different bilayer periods and thicknesses of the individual layers, were investigated. Two series of multilayers with different ratios between the thicknesses of TiN and ZrN layers (0.6 and 1.5, respectively) were prepared. Of each series, structures with bilayer periods in the micrometer (0.4 – 0.5 μm) and nanometer (3-4 nm) ranges were studied.

EDX measurements revealed that the TiN and ZrN layers were almost stoichiometric. XRD analysis exhibited a strong (111) preferred orientation both for the single layer and multilayer coatings. In the case of the multilayers, the relative intensities of the difraction peaks depended on the bilayer periods and on the thicknesses of the individual layers.

As compared with the monolayers, for the TiN/ZrN superlattice coatings an increase of the microhardness with 700 – 900 $HV_{0.03}$ was found, but no superhard coatings have been formed. In contrast, the adhesion for the multilayers was equal or even worse than that of the monolayers. The wear resistance tests revelead a significant increase (2.5 times) of the wear resistance of a multilayer coating (12 alternating layers) in comparison with that measured for TiN or ZrN single layer coatings.

Research in progress is devoted to a systematic investigation on the properties of the superlattice structured (Λ = 1 – 10 nm) hard coatings of TiN/ZrN and TiC/ZrC multilayer coatings.

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